Strategically Designed Anisotropic Organic-Inorganic Metal Halides (OIMHs) With Superior Balance Between Bandgap and Birefringence

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Table S1. Birefringence comparison between title compounds and some reported Pb^{2+}-based crystal.

Compounds	Birefringence (Δn)	Eg (eV)	Octahedra	Distortion degrees (Δd)	Ref.[c]
1	0.243 @ 550 nm[a]	4.23 eV	$CdNO_3I_2$	1.2×10^{-2}	This
2	0.388 @ 550 nm[a]	3.94 eV	CdN_2I_4	1.1×10^{-2}	work
$(C_2N_3H_4)_2PbCl_4$	0.18 @ 550 nm[a]	3.4 eV	$PbCl_6$	1.6×10^{-4}	45
$(C_{10}H_{11}N_3)PbCl_4$	0.046 @ 550 nm[a]	3.35 eV	$PbCl_6$	1.7×10^{-3}	46
$(C_{10}H_{11}N_3)PbBr_4$	0.127 @ 550 nm[a]	2.95 eV	$PbBr_6$	1.1×10^{-3}	46
$(C_4H_{10}NO)PbCl_3$	0.098 @ 1064 nm[b]	3.55 eV	$PbCl_6$	1.6×10^{-3}	47
$(C_4H_{10}NO)PbBr_3$	0.111 @ 1064 nm[b]	3.60 eV	$PbBr_6$	1.3×10^{-3}	47
$(C_3H_{10}N)PbI_3$	0.293 @ 1064 nm[b]	3.24 eV	PbI_6	4.7×10^{-4} [d]	48
$Cs_3Pb_2(CH_3COO)_2I_5$	0.26 @ 1064 nm[b]	2.55 eV	PbI_4O_2	1.4×10^{-2}	50
$Cs_3Pb_2(CH_3COO)_2Br_5$	0.15 @ 1064 nm[b]	3.26 eV	$PbBr_4O_2$	9.7×10^{-3}	50
$K_2I[PbI(OOCCH_2COO)]$	0.218 @ 546 nm[a]	3.34 eV	PbO_4I_2	1.5×10^{-2}	51
$(C_{12}H_9N_2)PbCl_3$	0.65 @ 546 nm[a]	2.38 eV	$PbCl_6$	1.8×10^{-3}	52
$(C_5N_{10}H_{10})_2PbI_7 \cdot H_2O$	0.49 @ 550 nm[a]	2.48 eV	PbI_6	1.4×10^{-3}	53
$(C_3H_8N_6)PbBr_4$	0.322 @ 550 nm[a]	3.13 eV	$PbBr_6$	1.8×10^{-3}	75
$(C_6N_{10}H_8)Pb_2Br_6$	0.42 @ 550 nm[a]	3.36 eV	$PbBr_6$	1.9×10^{-3}	76

a: experimental value; b: theoretical value; c: the references in the table refer to those in the main text, d: The structure contains five kinds of PbI_6 distorted octahedrons, the maximum of which is shown here.

Table S2. Crystallographic data.

Compound	1	2
empirical formula	$C_6H_6CdINO_3$	$C_{12}H_{10}CdI_2N_2O4$
formula weight	379.42	612.42
crystal system	triclinic	orthorhombic
space group	*P*-1	*Pnnm*
T (K)	300.00(10)	293(2)
a (Å)	7.51020(10)	23.174(2)
b (Å)	7.99360(10)	9.0285(10)
c (Å)	9.02660(10)	4.1289(4)
V (Å^3)	472.483(11)	863.89(15)
Z	2	2
ρ_{calc} (g/cm^3)	2.667	2.354
μ (mm^{-1})	43.950	4.851
goodness of fit on F^2	1.086	1.22

R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0274, 0.0710	0.0367, 0.0735
R_1, wR_2 (all data)[a]	0.0277, 0.0713	0.0436, 0.0754

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, and $wR_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$

Table S3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1** and **2**.

1

Atom	x	y	z	U(eq)
I1	7613.3(3)	4183.7(3)	3310.3(3)	33.31(13)
Cd1	7990.9(4)	3864.7(3)	6365.0(3)	29.74(13)
O1	8011(5)	12633(4)	8497(4)	42.6(7)
O2	7797(4)	10833(4)	6164(3)	36.0(6)
OW	4464(4)	2366(4)	6207(4)	38.2(6)
N1	7842(4)	6503(4)	7944(4)	26.1(6)
C1	7858(5)	11100(5)	7608(5)	29.5(8)
C6	7435(6)	6547(5)	9381(5)	32.2(8)
C2	7161(7)	8041(6)	10321(5)	38.4(9)
C3	7329(6)	9558(5)	9766(5)	32.1(8)
C4	7740(5)	9524(5)	8280(4)	25.2(7)
C5	8002(5)	7978(4)	7414(4)	25.6(7)

2

Atom	x	y	z	U(eq)
I1	4353.5(2)	6690.3(7)	5000	38.2(2)
Cd1	5000	5000	0	34.2(3)
O1	2540(3)	4231(10)	720(100)	112(13)
O2	2261(5)	2060(11)	1190(40)	106(9)
N1	4266(3)	3148(8)	0	36.8(17)
C1	3268(3)	2447(10)	0	42(2)
C2	3705(3)	3512(9)	0	39(2)
C3	2664(4)	2982(13)	400(300)	50(20)
C4	3427(4)	970(10)	0	47(2)
C5	3996(4)	617(10)	0	59(3)
C6	4407(3)	1723(10)	0	49(2)

Table S4. Bond Lengths for **1** and **2**.

1

Atom	Atom	Length/Å	Atom	Atom	Length/Å

I1	Cd1	2.8466(4)	O2	C1	1.264(5)
I1	Cd1[1]	2.9756(3)	N1	C6	1.337(5)
Cd1	O1[2]	2.369(3)	N1	C5	1.340(4)
Cd1	O2[2]	2.327(2)	C1	C4	1.499(5)
Cd1	OW	2.394(3)	C6	C2	1.381(6)
Cd1	N1	2.287(3)	C2	C3	1.383(6)
Cd1	C1[2]	2.681(3)	C3	C4	1.382(6)
O1	C1	1.247(5)	C4	C5	1.385(5)

[1]2-X,1-Y,1-Z; [2]+X,-1+Y,+Z

2

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	Cd1[1]	2.9725(4)	N1	C2	1.342(10)
I1	Cd1	2.9725(4)	N1	C6	1.327(11)
Cd1	N1[2]	2.385(6)	C1	C2	1.396(11)
Cd1	N1	2.385(6)	C1	C3[3]	1.49(2)
O1	C3[3]	1.26(5)	C1	C3	1.49(2)
O1	C3	1.17(2)	C1	C4	1.384(12)
O2	C3	1.29(4)	C4	C5	1.357(11)
O2	C3[3]	1.42(7)	C5	C6	1.379(12)

[1]+X,+Y,1+Z; [2]1-X,1-Y,-Z; [3]+X,+Y,-Z

Table S5. Bond Angles for **1** and **2**.

1

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cd1	I1	Cd1[1]	88.708(9)	N1	Cd1	C1[2]	117.86(11)
I1	Cd1	I1[1]	91.292(10)	C1[2]	Cd1	I1[1]	95.30(8)
O1[2]	Cd1	I1	162.92(7)	C1[2]	Cd1	I1	135.43(9)
O1[2]	Cd1	I1[1]	93.62(8)	C1	O1	Cd1[3]	90.2(2)
O1[2]	Cd1	OW	85.15(11)	C1	O2	Cd1[3]	91.7(2)
O1[2]	Cd1	C1[2]	27.73(11)	C6	N1	Cd1	120.8(2)
O2[2]	Cd1	I1[1]	95.24(7)	C6	N1	C5	118.2(3)
O2[2]	Cd1	I1	107.41(7)	C5	N1	Cd1	120.8(2)
O2[2]	Cd1	O1[2]	55.85(10)	O1	C1	O2	122.3(3)
O2[2]	Cd1	OW	85.66(10)	O1	C1	C4	118.6(4)
O2[2]	Cd1	C1[2]	28.13(11)	O2	C1	C4	119.1(3)
OW	Cd1	I1	90.44(7)	N1	C6	C2	122.4(3)
OW	Cd1	I1[1]	177.72(7)	C6	C2	C3	119.0(4)
OW	Cd1	C1[2]	84.51(10)	C4	C3	C2	119.1(3)

N1	Cd1	I1	105.73(8)	C3	C4	C1	121.0(3)
N1	Cd1	I1[1]	92.73(7)	C3	C4	C5	118.4(3)
N1	Cd1	O1[2]	90.38(10)	C5	C4	C1	120.7(3)
N1	Cd1	O2[2]	145.66(11)	N1	C5	C4	122.9(3)
N1	Cd1	OW	85.37(10)				

[1]2-X,1-Y,1-Z; [2]+X,-1+Y,+Z; [3]+X,1+Y,+Z

2

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cd1[1]	I1	Cd1	87.979(16)	C6	N1	C2	118.4(7)
I1	Cd1	I1[2]	92.022(16)	C2	C1	C3[5]	117.3(9)
I1[3]	Cd1	I1[4]	92.022(16)	C2	C1	C3	117.3(9)
I1	Cd1	I1[3]	180	C4	C1	C2	118.0(7)
I1[4]	Cd1	I1[2]	180.00(2)	C4	C1	C3[5]	124.2(9)
I1	Cd1	I1[4]	87.978(16)	C4	C1	C3	124.2(9)
I1[3]	Cd1	I1[2]	87.978(16)	N1	C2	C1	122.3(8)
N1	Cd1	I1[4]	90.04(11)	O1	C3	O2[5]	117(4)
N1[3]	Cd1	I1[2]	90.04(11)	O1	C3	O2	115(4)
N1[3]	Cd1	I1[3]	90.04(11)	O1[5]	C3	O2	120.4(18)
N1[3]	Cd1	I1[4]	89.96(11)	O1[5]	C3	O2[5]	102(6)
N1	Cd1	I1[3]	89.96(11)	O1[5]	C3	C1	118(5)
N1	Cd1	I1	90.04(11)	O1	C3	C1	123.8(10)
N1[3]	Cd1	I1	89.96(11)	O2	C3	C1	119.9(16)
N1	Cd1	I1[2]	89.96(11)	O2[5]	C3	C1	112(5)
N1	Cd1	N1[3]	180	C5	C4	C1	119.0(8)
C2	N1	Cd1	121.3(5)	C4	C5	C6	120.0(9)
C6	N1	Cd1	120.3(5)	N1	C6	C5	122.2(8)

[1]+X,+Y,1+Z; [2]1-X,1-Y,1-Z; [3]1-X,1-Y,-Z; [4]+X,+Y,-1+Z; [5]+X,+Y,-Z

Table S6. Hydrogen Bonds for **1** and **2**.

1

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
OW	HWA	O2[1]	0.85	1.91	2.737(4)	164.0

[1]1-X,1-Y,1-Z

2

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2	H2A	O1[1]	0.824(10)	2.65(6)	3.44(3)	160(14)

[1]1/2-X,-1/2+Y

Table S7. The assignments of the infrared absorption peaks for **1** and **2**.

Assignment (cm^{-1})	1	2
O-H	3502, 1609	3429
C-H	3059	3067
C=O	\	1654
C=C	1552	1615
C-O	1399	1393

Table S8. List of π-π interactions for **1**.

Cg(I)-Cg(J)	ARU(J)	Cg-Cg (Å)	Alpha (°)	Beta (°)	Gamma (°)	CgI_Perp (Å)	CgJ_Perp (Å)
Cg(4)-Cg(4)	a	5.707(2)	0.0(2)	59.6	59.6	2.8838(18)	2.8839(18)
Cg(4)-Cg(4)	b	3.773(2)	0.0(2)	21.7	21.7	3.5065(18)	3.5065(18)

a = 1-X, 1-Y, 2-Z; b = 2-X, 2-Y, 2-Z; Cg(I) = Plane number I (= ring number in () above); Alpha = Dihedral Angle between Planes I and J (Deg); Beta = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg); Gamma = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg); Cg-Cg = Distance between ring Centroids (Ang.); CgI_Perp = Perpendicular distance of Cg(I) on ring J (Ang.); CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Ang.)

Table S9. List of π-π interactions for **2**.

Cg(I)-Cg(J)	ARU(J)	Cg-Cg (Å)	Alpha (°)	Beta (°)	Gamma (°)	CgI_Perp (Å)	CgJ_Perp (Å)
Cg(3)-Cg(3)	a	4.1289(5)	0	0.00	0.00	4.1289	4.1289

a = X, Y, 1+Z.

Table S10. The Sn, Sb, and Bi based birefringent crystals shown in Figure 4.

Compounds	Birefringence	Eg (eV)	Ref.[b]
$[C(NH_2)_3]Sb(C_2O_4)F_2 \cdot H_2O$	0.323 @ 546 nm[a]	4.09	40
$MLASnCl_4$	0.294 @ 550 nm[a]	3.71	77
$(C_9H_{14}N)SbCl_4$	0.095 @ 546 nm[a]	3.47	78
$(C_8H_7N_2O_2)_6[Bi_2Cl_{10}]Cl_2 \cdot 2H_2O$	0.380 @ 550 nm[a]	3.22	79
$[C(NH_2)_3]BiCl_2SO_4$	0.143 @ 546 nm[a]	3.85	80

a: experimental value; b: the references in the table refer to those in the main text.

Table S11. Birefringence comparison between title compounds and several reported Cd-based crystals featuring octahedral structures.

Compounds	Birefringence (Δn)	Eg (eV)	Octahedra	Distortion degrees (Δd)	Ref.[c]
1	0.243 @ 550 nm[a]	4.23 eV	$CdNO_3I_2$	1.2×10^{-2}	This
2	0.388 @ 550 nm[a]	3.94 eV	CdN_2I_4	1.0×10^{-2}	work
$Cd(H_2C_6N_7O_3)2{\cdot}8H_2O$	0.60 @ 550 nm[a]	4.0 eV	CdO_5N	2.5×10^{-4}	42
$Cd_2Nb_2Te_4O_{15}$	0.12 @ 546 nm[a]	3.75 eV	CdO_6	9.28×10^{-3}	81
$Cd(NH_2SO_3)_2{\cdot}2H_2O$	0.052 @ 1064 nm[b]	5.09 eV	CdN_2O_4	5.1×10^{-4}	55
$Cd(SCN)_2(CH_4N_2S)_2$	0.35 @ 546 nm[a]	3.90 eV	CdN_2S_4	8.5×10^{-3}	56
Cd(OH)Cl	0.042 @ 546 nm[a]	4.55 eV	CdO_3Cl_3	8.3×10^{-3}	83
$C(NH_2)_3Cd(C_2O_4)Cl(H_2O){\cdot}H_2O$	0.075 @ 1064 nm[b]	3.76 eV	CdO_5Cl	9.7×10^{-4}	85
$BaCd(C_2O_4)_{1.5}Cl(H_2O)_2$	0.096 @ 1064 nm[b]	4.53 eV	CdO_5Cl	1.6×10^{-3}	85
$(C_4H_{10}NO)_2Cd_2Cl_6$	0.03 @ 1064 nm[b]	5.45 eV	$CdCl_6$/ CdO_2Cl_4	1.3×10^{-3}/ 8.6×10^{-5}	86
$[(CH_3)_3NCH_2Cl]CdCl_3$	0.044 @ 1064 nm[b]	5.24 eV	$CdCl_6$	6.6×10^{-5}	87

a: experimental value; b: theoretical value; c: the references in the table refer to those in the main text.

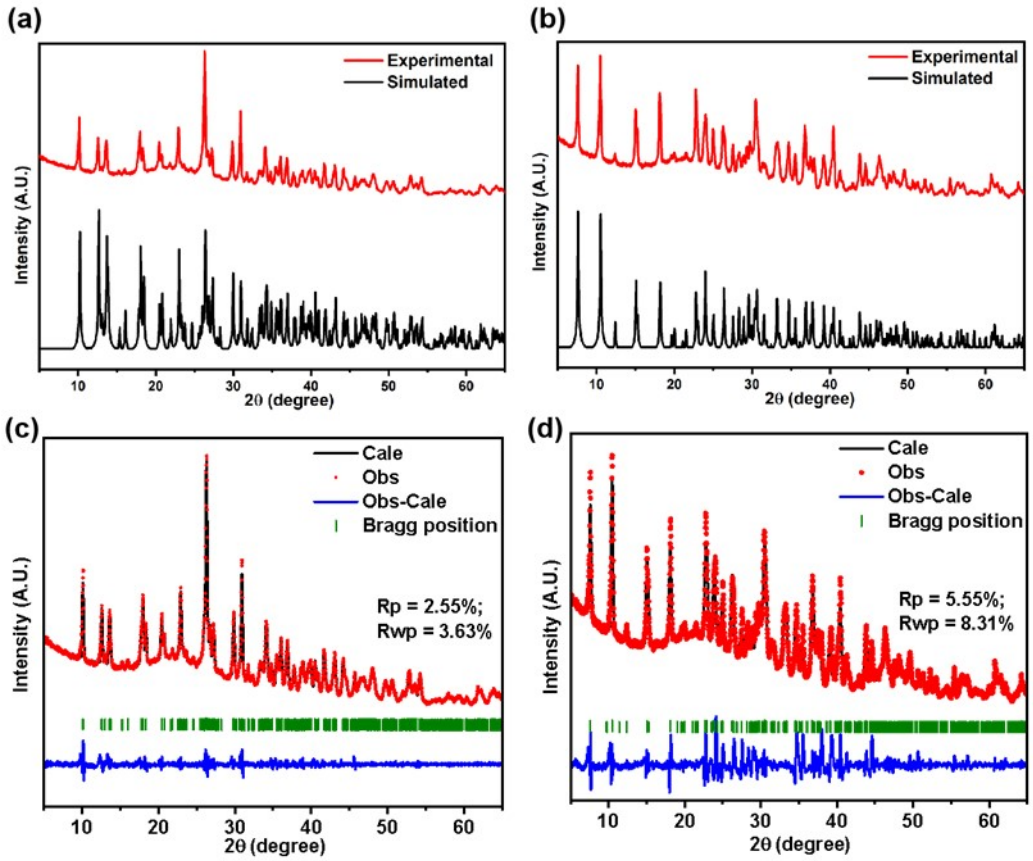

Figure S1. Simulated and measured powder X-ray diffraction patterns for **1** (a) and **2** (b); refined PXRD data for 1(c) and 2(d).

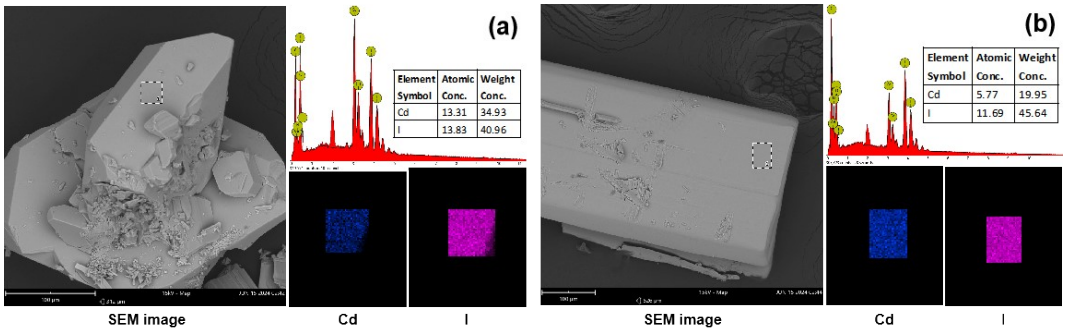

Figure S2. SEM images for **1** (a) and **2** (b).

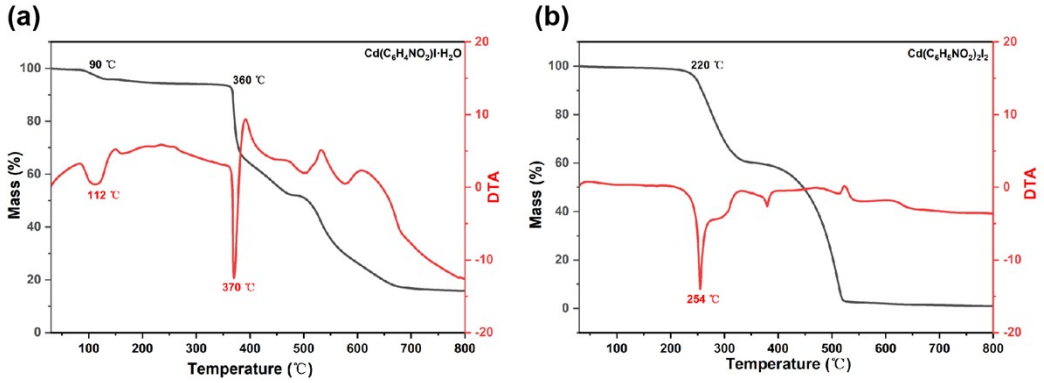

Figure S3. TG and DTA for **1** (a) and **2** (b).

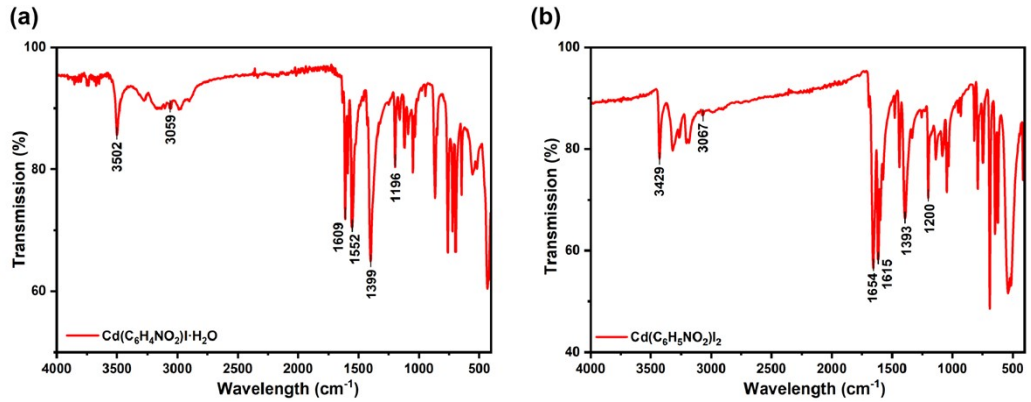

Figure S4. IR spectra of **1** (a) and **2** (b).

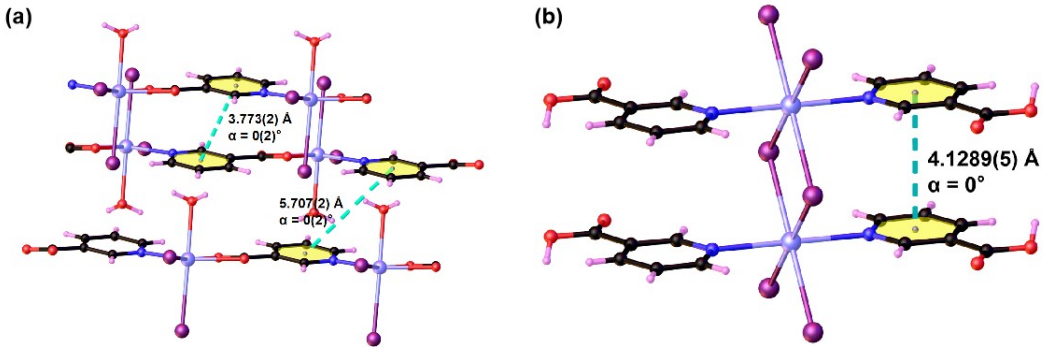

Figure S5. The π-π interactions in **1** (a) and **2** (b).

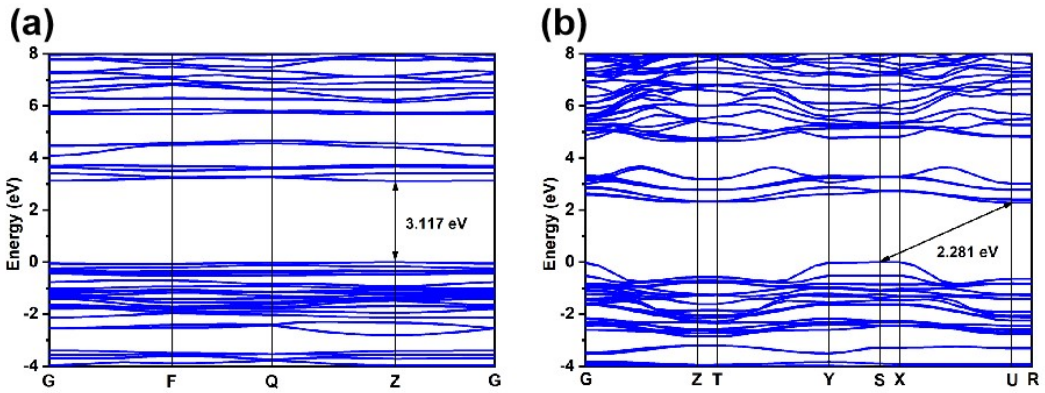

Figure S6. The calculated band structures of **1** (a) and **2** (b)

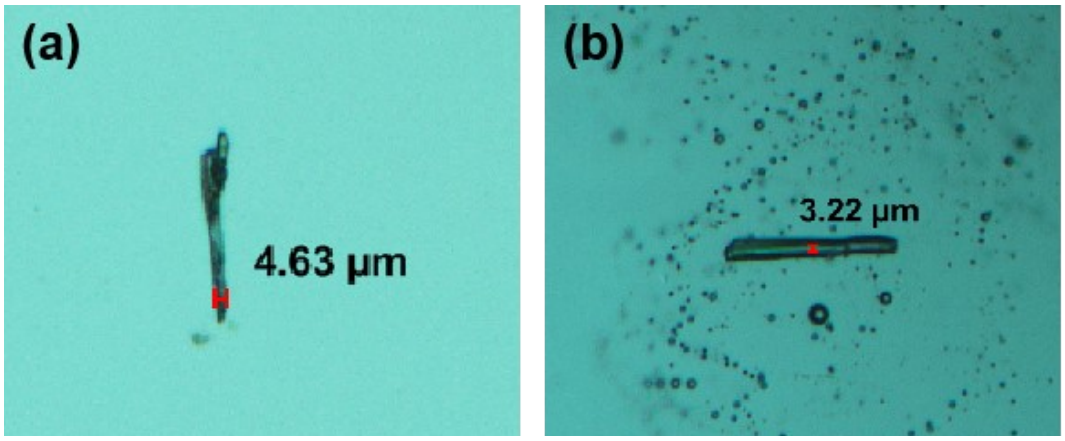

Figure S7. The thickness of **1** (a) and **2** (b) crystals used for birefringence measurements.